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Residence Times of Reflected Brownian Motion

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1. Introduction

In the course of diffusive motion, each species explores different regions of the bulk. Since reactive zones are often heterogeneously distributed in the bulk (e.g., in chemical reactor or biological cell), the net outcome and the whole functioning of the system strongly depend on how long the diffusing species remains in these zones. These so-called residence or occupation times are relevant for various diffusion influenced reactions e.g., energy transfer or fluorescence quenching [1]. In most cases, the motion of diffusing species is restricted by a geometrical confinement, resulting in drastic modifications of the transport. The resulting process is known as reflected Brownian motion [2]. Here, we propose a general solution to the problem of finding the probability distribution of its residence times [3].

2. Eigenmode expansion

For a given function $B(\boldsymbol{r})$ in a bounded domain Ω with a smooth boundary $\partial\Omega$, we consider the random variable

$$\varphi = \int_0^t ds\, B(X_s)$$

X_s being a random trajectory of the reflected Brownian motion in Ω, started with a given initial density $\rho(\boldsymbol{r})$. Intuitively, the function $B(\boldsymbol{r})$ can be considered as a distribution of "markers" to distinguish different points or regions of the confining domain. When the diffusing species passes through these regions, the random variable φ accumulates the corresponding "marks". In other words, different parts of the trajectory are weighted according to the function $B(\boldsymbol{r})$, "encoding" thus the whole stochastic process.

The classical Kac's result [4] allows one to relate the statistics of φ to a solution $w(\boldsymbol{r}, t)$ of the diffusion equation

$$[\partial_t - \Delta + hB(\boldsymbol{r})]\, w(\boldsymbol{r}, t) = 0 \quad \text{(in the bulk)}$$

with the Neumann boundary condition $\partial_n w(\boldsymbol{r}, t) = 0$ at the boundary $\partial\Omega$, the initial condition $w(\boldsymbol{r}, t=0) = \rho(\boldsymbol{r})$, and a positive constant h. The Laplace transform of the probability distribution of φ is then

$$\boldsymbol{E}\{\exp(-h\varphi)\} = \int_\Omega d\boldsymbol{r}\, w(\boldsymbol{r}, t)\, \rho_a(\boldsymbol{r})$$

where the expectation includes the average of the functional $\exp(-h\varphi)$ over all random trajectories $\{X_s\}_{0\le s\le t}$ of the reflected Brownian motion between the starting point $\boldsymbol{r}_0$ at time 0 and the arrival vicinity of point $\boldsymbol{r}$ at time t, as well as the average over all $\boldsymbol{r}_0$ and $\boldsymbol{r}$ with given initial and arrival densities $\rho(\boldsymbol{r}_0)$ and $\rho_a(\boldsymbol{r})$, respectively.

Expansion of the solution $w(\boldsymbol{r}, t)$ over the complete orthonormal basis of the Laplace operator eigenfunctions $u_m(\boldsymbol{r})$ reduces the problem to a set of ordinary differential equations for the unknown coefficients $c_m(t)$. Thinking of $c_m(t)$ as components of an

infinite-dimensional vector, one finds the solution of these equations that yields a compact matrix form of a scalar product for the expectation:

$$\boldsymbol{E}\{\exp(-h\varphi)\} = (\mathrm{U}\exp[-(h\boldsymbol{B}+\boldsymbol{\Lambda})t]\,\mathrm{U}') \qquad (1)$$

where the infinite-dimensional matrices $\boldsymbol{B}$ and $\boldsymbol{\Lambda}$ and vectors U and U' are

$$\boldsymbol{B}_{\mathrm{m,m'}} = \int_{\Omega} d\boldsymbol{r}\, u_{\mathrm{m}}^{*}(\boldsymbol{r})\, B(\boldsymbol{r})\, u_{\mathrm{m'}}(\boldsymbol{r}) \qquad \boldsymbol{\Lambda}_{\mathrm{m,m'}} = \delta_{\mathrm{m,m'}}\,\lambda_{\mathrm{m}}$$

$$\mathrm{U}_{\mathrm{m}} = V^{1/2}\int_{\Omega} d\boldsymbol{r}\, u_{\mathrm{m}}^{*}(\mathbf{r})\,\rho(\boldsymbol{r}) \qquad \mathrm{U'}_{\mathrm{m}} = V^{1/2}\int_{\Omega} d\boldsymbol{r}\, u_{\mathrm{m}}(\boldsymbol{r})\,\rho_{\mathrm{a}}(\boldsymbol{r})$$

λ_{m} being the Laplace operator eigenvalues, and V the volume of the domain. Note that a formal substitution of $h = -iq$ into Eq. (1) gives the characteristic function of φ. Its inverse Fourier transform yields the probability distribution of φ, while the series expansion of $\exp(iq\varphi)$ generates all its moments.

If A is a subset of the confining domain Ω and $B(\boldsymbol{r})$ is taken to be the indicator of A ($I_A(\boldsymbol{r}) = 1$ for $\boldsymbol{r}$ in A, and 0 otherwise), the random variable φ is the residence time showing how long the diffusing species resides onto this subset. The indicator function $I_A(\boldsymbol{r})$ can be thought of as a "counter" which is turned on whenever the diffusing species resides in A. One can estimate for instance the "trapping" time that particles spend in deep and almost enclosed pores (like fjords) of a catalyst.

The closed matrix form (1) is the central result. It provides a complete probabilistic description of the random variable φ. In addition, this matrix representation allows one to study the moments of φ in detail (not presented, see [3]). Most importantly, the present approach is efficient for numerical calculation of the residence times. The increase of eigenvalues λ_{m} enables one to truncate both matrices $\boldsymbol{\Lambda}$ and $\boldsymbol{B}$ to moderate sizes, allowing rapid and very accurate computation of the matrix exponentials in Eq. (1), in comparison to conventional methods like Monte Carlo simulations (see Ref. [2] for the use of similar matrix formalism in nuclear magnetic resonance).

3. Conclusion

We proposed a general solution to the problem of finding the probability distribution of residence times of a Brownian particle confined by reflecting boundaries. The Fourier and Laplace transforms of this distribution were derived in a compact matrix form involving the Laplace operator eigenbasis. When the eigenbasis (or its part) is known, the numerical computation of the residence time is straightforward and very accurate. The present approach can also be applied to investigate other functionals of reflected Brownian motion describing, in particular, restricted diffusion in an external field or potential (e.g., nuclei diffusing in an inhomogeneous magnetic field [2]). The developed concepts can be extended to more complicated stochastic processes governed by a general second-order elliptic differential operator having a complete eigenbasis.

References

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